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# Time Reversal of the Overdamped Langevin Equation and Fixman's Law

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We show that the first order Langevin equation for the overdamped dynamics of an interacting system has a natural time reversal of simple but surprising form. This leads to a clear derivation of Fixman's relation for how interactions modify the time dependent response of the system, and we show the application to the time dependent diffusion of dilute polymer coils. We find the generalized "Fixman Law" for dissipation with a memory kernel, and we also discuss the case of the second order Langevin Equation.

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Our starting point is a background system in thermal equilibrium at temperature  $T$ , a minority of whose degrees of freedom are given by  $x_i(t)$ . If we apply small enough additional forces  $F_i(t)$  to these degrees of freedom, then the classical Fluctuation-Dissipation Theorem leads to the Langevin model for their dynamics as

$$\frac{dx_i}{dt} = \int^t dt' G_{ij}^{(+)}(t-t') F_j(t') + u_i(t) \quad (1)$$

where

$$k_B T G_{ij}(t-t') = \langle u_i(t) u_j(t') \rangle \quad (2)$$

are the velocity fluctuations measured in the undriven system and  $G_{ij}^{(+)}(t-t') = \theta(t-t') G_{ij}(t-t')$  is the strictly causal part of  $G$ .

The above becomes the Langevin Equation for an interacting system if we take the forces  $F_i(t) = f_i(x(t))$  to be conservative interactions layered on top of the underlying equilibrium system. For example the  $x_i$  and added forces might be the coordinates of colloidal particles interacting due to added surface charges, or the coordinates of (sub-)molecules experiencing the connecting bond forces of a polymer chain. Notice that this interpretation would imply inertial effects are already subsumed in the  $G_{ij}(t)$  (although we will revisit this later).

We obtain simple results by focussing on the case where there is sufficient separation of timescales to take  $G_{ij}^{(+)}(t-t') = M_{ij} \delta(t-t')$  where  $M_{ij}$  is an instantaneous mobility and correspondingly  $G_{ij}(t-t') = 2M_{ij} \delta(t-t')$ . Our Langevin Equation then becomes

$$\frac{dx_i}{dt} = M_{ij} f_j(x(t)) + u_i(t). \quad (3)$$

We now seek a time reversal of this equation with  $t^R = -t$  and  $x^R(t^R) = x(t)$  obeying

$$\frac{dx_i^R}{dt^R} = M_{ij} f_j(x^R(t^R)) + u_i^R(t^R) \quad (4)$$

which requires that the time reversal of the random velocity contribution be given by

$$u_i^R(t_R) = -u_i(t) - 2M_{ij} f_j(x(t)). \quad (5)$$

At first sight the second term above is puzzling because the random velocity should be unbiased, but this is conditional on the past:  $u(t)$  is independent of past  $x(t' < t)$ . Correspondingly  $u_R(t_R)$  should be independent of future  $x(t' > t)$  and the difference of condition matters because  $x(t' > t)$  clearly cumulates influence from the earlier random velocity terms  $u(t)$ .

Useful correlation identities follow from the above by considering that for  $t^R > t'^R$  we should have  $\langle u_i^R(t_R) v_j^R(t'_R) \rangle = 0$  where  $v_i^R(t_R) = v_i(t) = M_{ij} f_j(x(t))$  is the velocity response to the conservative forces. Substituting back in terms of unreversed quantities then leads to

$$\langle u_i(t) v_j(t') \rangle = -2 \langle v_i(t) v_j(t') \rangle, \quad t < t' \quad (6)$$

whereas this correlation is zero for  $t > t'$ . From this the response function of the interacting system  $G_{ij}^{\text{int}}(t-t') = \langle \dot{x}_i(t) x_j(t') \rangle / (k_B T)$  can be expressed as

$$G_{ij}^{\text{int}}(t-t') = G_{ij}(t-t') - \langle v_i(t) v_j(t') \rangle / (k_B T). \quad (7)$$

The above follows by substituting  $dx_i/dt = v_i(t) + u_i(t)$  and using our relation further above to eliminate cross terms.

The above result was first obtained by Fixman by Diffusion Equation arguments [7, 8], in the polymer context which we discuss below, but in a manner which did not convince later authors albeit they found some numerical evidence to support it when  $t \simeq t'$  [9]. Its power is that it expresses the diffusion of the interacting system in terms of the bare non-interacting value *minus* a restraining contribution from the additional forces.

## APPLICATION TO POLYMER DIFFUSION

The archetypal application is to the motion of colloid and polymer systems in a Newtonian solvent, where the  $x_i(t)$  are the  $3N$  coordinates of  $N$  particle position vectors  $\vec{r}_n(t)$  and the joint mobility tensor is that of Oseen with  $M \rightarrow O_{mn} = \frac{1}{8\pi\eta r_{mn}} (I + \hat{r}\hat{r})$  for off-diagonal blocks  $m \neq n$  and diagonal blocks given by  $O_{nn} = \frac{1}{6\pi\eta a_n} I$ . For an isolated polymer coil of  $N$  beads equation ( ) then becomes

$$\langle \dot{\vec{r}}_n(t) \dot{\vec{r}}_m(t') \rangle = 2O_{mn}\delta(t-t') - \langle \vec{v}_n(t) \vec{v}_m(t') \rangle \quad (8)$$

where the leading term is Kirkwood's approximation and all the time dependent memory is captured in the counter terms correlating the velocity contribution

$$\vec{v}_m(t) = \sum_n O_{mn} \cdot \vec{F}_n(t) \quad (9)$$

which is driven by the conservative forces holding the polymer chain together. Focussing for simplicity on the coil centre of mass  $\vec{R}(t) = \sum_n \vec{r}_n(t)/N$ , the corresponding velocity autocorrelation function is then given by

$$A(t-t') = \langle \vec{V}(t) \vec{V}(t') \rangle = 2D_K\delta(t-t') - A_F(t-t') \quad (10)$$

where  $D_K = N^{-2} \sum_{mn} \langle O_{mn} \rangle$  is the classical Kirkwood diffusivity and all the memory in the polymer centre of mass motion comes from the Fixman term

$$A_F(t-t') = N^{-2} \sum_{mm'n'} \langle O_{mm'}(t) \cdot \vec{F}_{m'}(t) \vec{F}_{n'}(t') \cdot O_{n'n}(t') \rangle. \quad (11)$$

The long time polymer coil diffusivity is then given by

$$D_L = D_K - \Delta = D_K - \int_0^\infty A_F(\tau) d\tau$$

and given that  $D_L$  is the natural experimental measurement whilst  $D_K$  is a direct configurational moment, it is important to understand their difference  $\Delta$  all arising from the Fixman term.

In Fig. 1 we show the time-dependence of  $A_F(t)$  in Gaussian and swollen chains measured in Wavelet Monte Carlo dynamics simulations [10][?]. In each case the longer time data is tolerably consistent with the natural scaling form  $A_F(t) = (R_e/\tau_Z)^2 h(t/\tau_Z)$  as plotted where we have used the rms chain end-to-end radius  $R_e \sim N^\nu$  as the natural scale of length and measured values of the relaxation time  $\tau_Z$  of the longest Rouse mode as the natural scale of time, and this behaviour on its own would lead to a contribution to  $\Delta$  proportional to  $R_e^2/\tau_Z \propto D_K$ . We also see short time structure  $A_F(t) = g(N)f(t)$  to times of order unity which on its own would lead to a contribution to  $\Delta$  proportional to  $g(N)$ , and for the

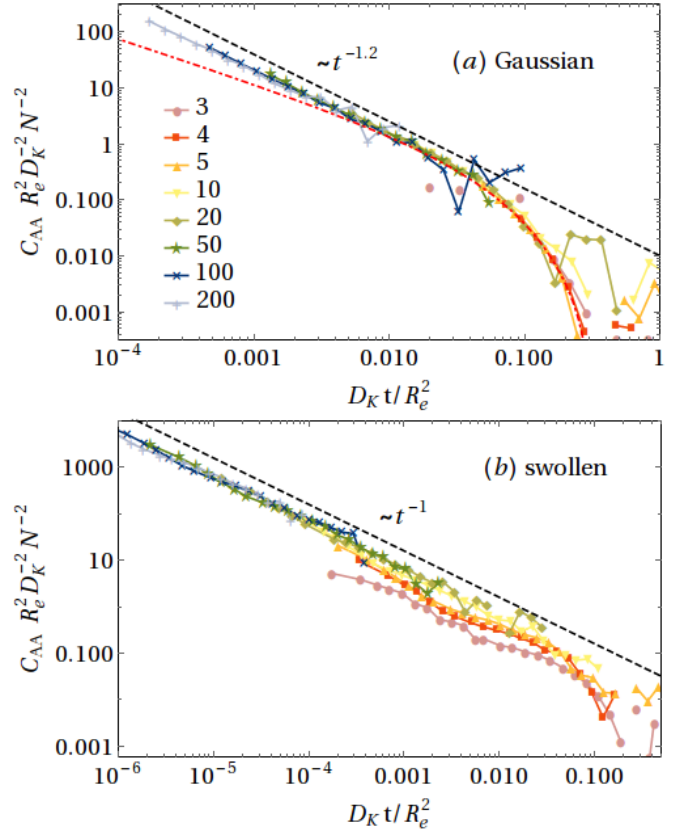


FIG. 1. Unscaled autocorrelation of  $\mathbf{A}$  against time scaled by a surrogate for the Zimm time (both scale as  $\sim N^{3\nu}$ ). The dashed curves indicate the gradient of the line onto which the curves of different  $N$  collapse, with the power calculated as the powers in Fig. ?? divided by  $3\nu$ .

particular case  $t = 0$  earlier work [9] showed that  $g(N)$  does appear to approach  $1/N$  albeit slowly.

In Fig. we show the corresponding cumulative integrals for  $\Delta(t) = \int_0^t A_F(t') dt'$  in scaled variables, as far as we can measure them above noise. Assuming these plots do go far enough to capture all the short time parts, the total values of  $\Delta_N/D_K$  inclusive of the scaling parts are estimated by finding the vertical shifts to align to a master curve in the scaled variables with plateau value zero, as shown in the third panel.

The measured estimates of  $\Delta_N/D_K$  are shown in Fig. THREE plotted against the anticipated correction to scaling which is  $N^{-1}/R^{-1} \propto N^{\nu-1}$ . These enable us to give the first quantitative estimates of the asymptotic values for true long time diffusion coefficient compared to the Kirkwood short time formula,

$$\frac{D - D_K}{D_K} = - \left( \frac{\Delta}{D_K} \right)_{N \rightarrow \infty} = \begin{cases} -3.3 \pm 0.3\% & \text{good solvent} \\ -9.1 \pm 0.2\% & \text{phantom chains.} \end{cases}$$

$$\frac{D - D_K}{D_K} = -\Delta_\infty = \begin{cases} -3.3 \pm 0.3\% & \text{good solvent} \\ -9.1 \pm 0.2\% & \text{phantom chains.} \end{cases}$$

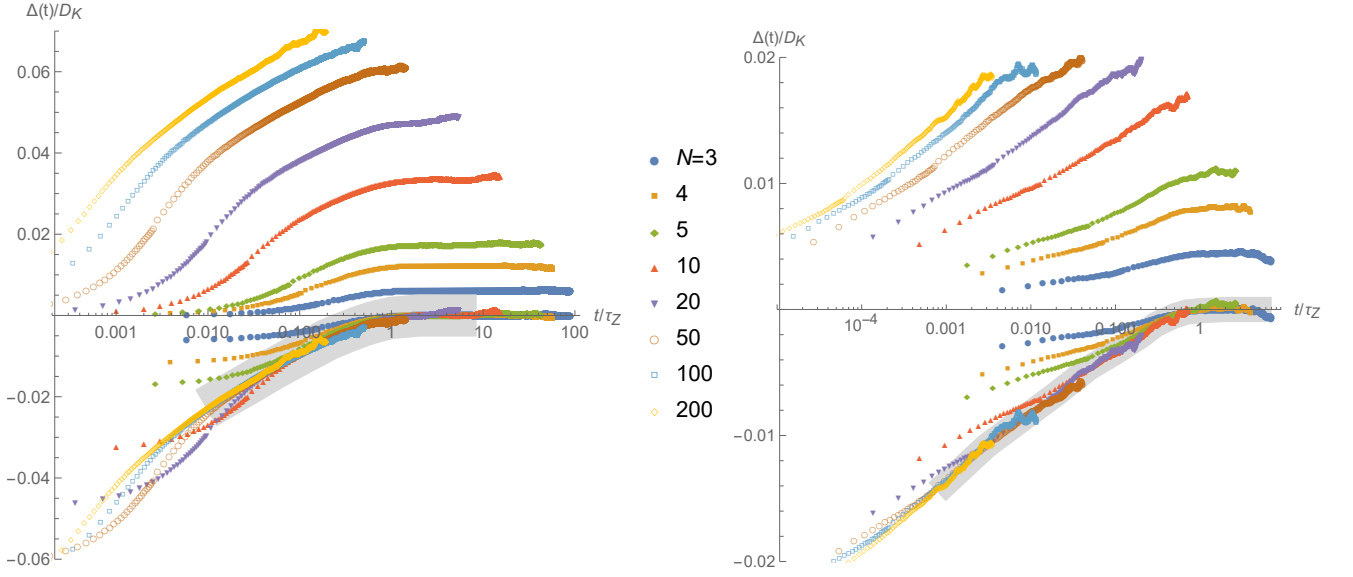


FIG. 2. Upper curves: fractional decrease in diffusivity, found by numerically integrating the data in Fig. ??? for the autocorrelation function  $A_F(t)$ , plotted against the upper time limit of integration, for various chain lengths  $N$ . Data has been truncated when noise begins to dominate additional contributions leading to incomplete curves, especially in (b) for swollen chains. The lower curves show the same data shifted vertically to a common master curve, with plateau value zero and shown in gray, the shift for each curve then giving an estimate of the eventual long time plateau of the relative decrease in diffusivity. Fig. 4

in the Supplementary Material gives a different presentation of these master curves.

These corrections intrude wherever a measured chain diffusivity or mobility, such as might be observed by dynamic light scattering or sedimentation respectively, is compared with the Kirkwood formula given in terms of configurational statistics. Direct determination of these corrections from simulation without use of the Fixman law would be very hard, as this would require direct measurement of  $D$  to better than 1% which would entail simulation (with full hydrodynamics included) far in excess of  $10^4$  chain relaxation times for each chain length. Direct determination by experiment would face the added difficulties of determining the configurational statistics to better than 1% and controlling any influence of polydispersity.

## SECOND ORDER LANGEVIN EQUATION

The basis for the second order langevin equation is slightly different, but it leads to a matching time reversal result. Our starting point is the random forces  $\phi_i(t)$  with observed autocorrelation  $\langle \phi_i(t)\phi_j(t') \rangle = 2k_B T Z_{ij} \delta(t-t')$  which are conjugate to a subset of variables  $x_i(t)$  of the underlying bath which are held (almost) stationary. Now attaching both conservative forces and inertia tensor  $m_{ij}$  to these degrees of freedom leads to the second order Langevin equation

$$m_{ij} \frac{d^2 x_j}{dt^2} + Z_{ij} \frac{dx_j}{dt} = f_i(x(t)) + \phi_i(t). \quad (12)$$

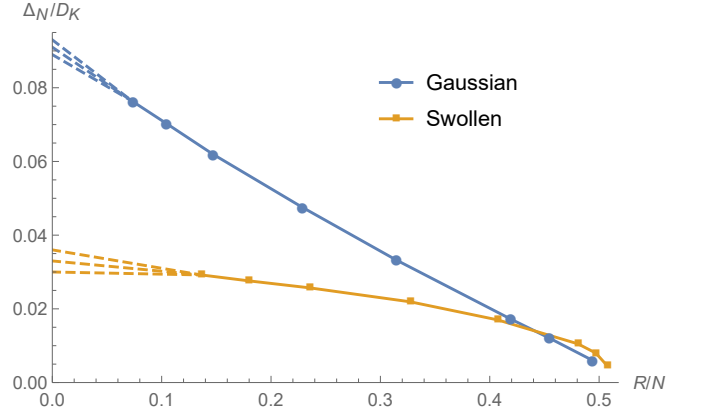


FIG. 3. Plateau values of  $\Delta/D_K$  for different chain lengths, plotted against the correction to scaling variable  $R/N$ . For both gaussian and swollen chains these show good straight line plots with extrapolated values and error ranges for  $n \rightarrow \infty$  indicated by the dashed lines with values shown in Eqn . The strong curvature of the swollen chain plot at small  $N$  comes mainly from non-scaling of the rms end-to-end radius used.

We now pose the analogous time reversed equation

$$m_{ij} \frac{d^2 x_j^R}{(dt^R)^2} + Z_{ij} \frac{dx_j^R}{dt^R} = f_i(x^R(t^R)) + \phi_i^R(t^R), \quad (13)$$

with  $x^R(t_R = -t) = x(t)$  as before, and by inspection this requires

$$\phi_i^R(t^R) = \phi_i(t) - 2Z_{ij} \frac{dx_j}{dt}. \quad (14)$$

This looks quite different from the first order case, but it turns out to exactly agree in the limit of inertia being negligible. Multiplying through by the mobility matrix  $Z^{-1}$  to obtain the random currents, and eliminating  $\frac{dx}{dt}$  using just the first order Langevin equation (3) leads back to the time reversal of the random currents as before (5).

## GENERALISATION TO MEMORY MEDIA

Finally we have considered the generalisation to first order Langevin equation for motion in a time dependent (or memory) medium, seeking insight into the status of Fixman's law in relation to other fluctuation-dissipation type results. We start from

$$\dot{x}(t) = \int G(t-t')f(x(t'))dt' + u(t) = G * f + u$$

where for causality  $G(t-t') = 0$  for  $t < t'$  and we will also allow ourselves the shorthand notation  $f(t) = f(x(t))$ . We leave indices implicit now but for the multivariate case  $G$  is a matrix, in terms of which

$$\langle u(t)u^T(t') \rangle = kT (G(t-t') + G^T(t'-t)).$$

## Time Reversal Symmetry

If we simply negate all time arguments to  $t_R = -t$  our equation of motion becomes  $-dx_R/dt_R = G_R * f_R + u(-t_R)$ , where  $x_R(t_R) = x(t) = x(-t_R)$  and similarly for  $f_R$  and  $G_R \equiv G_R(t_R) = G(t) = G(-t_R)$ . This matches the natural time reverse equation

$$dx_R/dt_R = G * f_R + u_R(t_R),$$

by taking

$$u_R(t_R) = -u(-t_R) - (G + G_R) * f_R.$$

This important complication is that we now have both causal  $G * f_R$  and anti-causal  $G_R * f_R$  propagation from the conservative forces entering our time reversal and results from it.

We show in the supplementary material that from the above it follows at some length that

$$\langle u f^T \rangle = -(G + G_R) * \langle f f^T \rangle_-$$

where

$$\langle f(t)f^T(t') \rangle_- = \begin{cases} -\langle f f^T \rangle & t < t' \\ 0 & t > t' \end{cases}.$$

It is then a matter of straightforward substitution to find

$$\begin{aligned} A_F(t-t') &= \langle \dot{x} \dot{x}^T \rangle_{\text{free}} - \langle \dot{x} \dot{x}^T \rangle \\ &= G_R * \langle f f^T \rangle_- * G_R + G * \langle f f^T \rangle_+ * G. \end{aligned} \quad (15)$$

This final memory medium version of Fixman's law is clearly new and different. Specialising to  $t > t'$  for clarity,  $A_F(t-t')$  can be expressed as

$$\int_{u>u'} du du' \langle G(t-u) \cdot f(u) (G_R(t'-u') \cdot f(u'))^T \rangle$$

which is the correlation of the causal response to the applied causal forces with the corresponding anti-causal response, with the added restriction that only causally ordered factors of forces contribute. This can be computed given observations of the force autocorrelation function  $\langle f f^T \rangle$  and knowledge of  $G$ , but it is certainly quite different from conventional Fluctuation-Dissipation Theorem type results.

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## SUPPLEMENTARY MATERIAL

Our general equation of motion is

$$\dot{x}(t) = \int G(t-t')f(x(t'))dt' + u(t)$$

where for causality  $G(t-t') = 0$ ,  $t < t'$  and we will also allow ourselves the shorthand notation  $f(t) = f(x(t))$ .

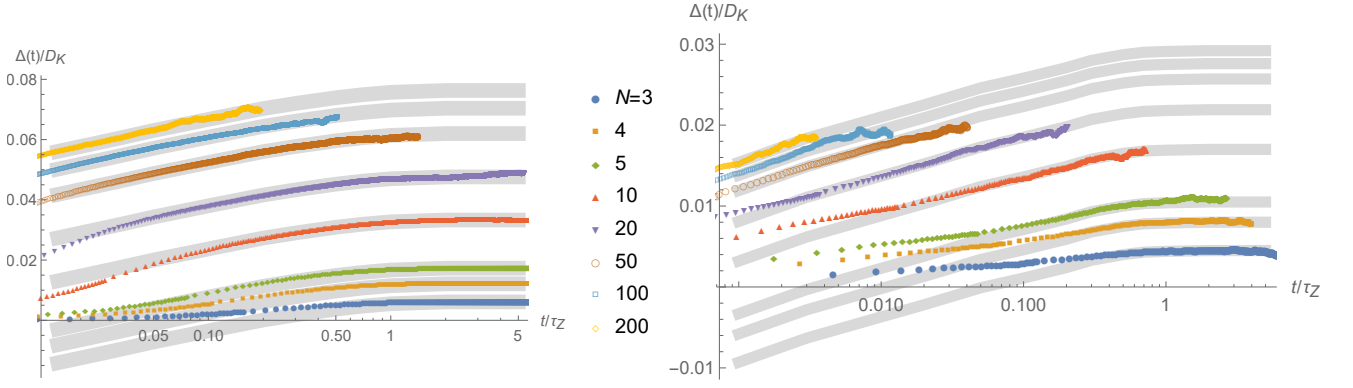


FIG. 4. Fractional decrease in diffusivity, found by numerically integrating the data in Fig. ??? for the autocorrelation function  $A_F(t)$ , plotted against the upper time limit of integration, for various chain lengths  $N$ . Master curves shown in gray were obtained by vertical linear shift of the data in the long time regime, and these are shown in gray behind (and extending) the curves for each  $N$ . The shifted master curves then give an estimate of the eventual long time plateau of the relative decrease in diffusivity for each curve.

For the multivariate case, that is where  $x$ ,  $f$  and  $u$  all become time dependent vectors, the above displayed equation applies with  $G$  being a matrix which for reversible background dynamics is symmetric, and we have  $\langle u(t)u^T(t') \rangle = kT (G(t-t') + G^T(t'-t))$ .

It proves useful to express the random velocity contributions as

$$u(t) = \int K(t-t')h(t')dt'$$

where  $\langle h(t)h^T(t') \rangle = \delta(t-t')\mathbf{1}$  is white noise and  $K(t-t') = 0$  for  $t < t'$  is strictly causal. Then we can interpret  $h(t)$  as the innovation, that is what is new in the noise at time  $t$ , with the important consequence that  $h(t)$  is uncorrelated with everything from earlier times,

$$\langle h(t)f^T(t') \rangle = 0, \quad t > t'. \quad (16)$$

The defining property of  $K$  is that the autocorrelation of  $u(t)$  reconstructs correctly, so we require  $kT (G(t-t') + G^T(t'-t)) = \int K(t-t'')K^T(t'-t'')dt''$ .

These equations have a natural time convolution structure, starting with

$$dx/dt = G * f + K * h.$$

We will use  $R$  to denote negation of time arguments, equivalent in effect to a transpose of the times as indices. Then we can write

$$\langle uu^T \rangle = kT (G + G_R^T) = K * K_R^T. \quad (17)$$

### Time Reversal Symmetry

If we simply negate all time arguments to  $t_R = -t$  in our equation of motion we obtain

$$-dx_R/dt_R = G_R * f_R + K_R * h_R.$$

Here  $x_R(t_R) = x(t) = x(-t_R)$  and similarly for  $f_R$  and  $h_R$ , whilst  $G_R \equiv G_R(t_R) = G(t) = G(-t_R)$  and similarly for  $K_R$ . The form of the equation of motion is clearly not preserved under this simple time negation, but if we allow a more complex time reversal mapping for the innovation under which  $h \rightarrow R[h]$  we can write

$$dx_R/dt_R = G * f_R + K * R[h],$$

which agrees with the original equation provided  $K * R[h] = -(G + G_R) * f_R - K_R * h_R$  leading to

$$R[h] = -K^{-1} (G + G_R) * f_R - K^{-1} * K_R * h_R.$$

Now we can use this to find a time reversed partner to eqn 16, which is that  $\langle R[h](t_R)f_R^T(t'_R) \rangle = 0$  for  $t_R > t'_R$ . This can in turn be time negated to  $\langle R[h]_R(t)f^T(t') \rangle = 0$  for  $t < t'$  where  $R[h]_R = -K_R * (G + G_R) * f - K_R^{-1} * K * h$  leading to

$$K_R^{-1} * K * \langle hf^T \rangle = -K_R * (G + G_R) * \langle ff^T \rangle \quad \text{for } t < t'. \quad (18)$$

### The cross correlation of $h$ and $f$ for reversible underlying

We now seek to bring equations 16 and 18 together as a single expression for  $\langle hf^T \rangle$ . This can be done in closed form for the case where the underlying dynamics is reversible, so that  $(G + G_R)_R = (G + G_R^T)$  from which it follows that  $G = G^T$  and  $G_R = G_R^T$ . In terms of  $K$  this leads to  $K * K_R^T = K_R * K^T$  and hence  $K_R^{-1} * K = K^T * (K_R^T)^{-1}$ , which can be substituted on the LHS of Eqn (18). We can also convolve both sides of the latter by  $(K^T)^{-1}$  which being causal preserves the time inequality, leading after some simplifications to the top line in

$$(K_R^T)^{-1} * \langle hf^T \rangle(t, t') = \begin{cases} -\langle ff^T \rangle & t < t' \\ 0 & t > t' \end{cases}.$$

The bottom line of the above follows simply by convolving Eq (16) by  $(K_R^T)^{-1}$  which being anticausal preserves its time inequality. Finally it is convenient to denote the joint RHS above as  $-\langle ff^T \rangle_-$  and then write the whole relation as  $\langle hf^T \rangle = -K_R^T * \langle ff^T \rangle_-$  and hence

$$\langle uf^T \rangle = -(G + G_R^T) * \langle ff^T \rangle_-$$

### Application to correlation function

Now we come to the heart of the matter and consider

$$\begin{aligned} \langle \dot{x} \dot{x}^T \rangle &= \langle uu^T \rangle + G * \langle ff^T \rangle * G_R^T \\ &\quad + \langle uf^T \rangle * G_R^T + G * \langle fu^T \rangle \end{aligned} \quad (19)$$

where the first term direct from the innovation auto-correlation corresponds to the “free” value of the LHS in the absence of any internal forces  $f$ . In the third term

we can substituted  $\langle uf^T \rangle$  using the previous subsection to give

$$\langle uf^T \rangle * G_R^T = -(G + G_R^T) * \langle ff^T \rangle_- * G_R^T \quad (20)$$

and the fourth term is this both transposed and time reversed for which we need to note  $\left(\langle ff^T \rangle_-\right)_R^T = \langle ff^T \rangle_+$  where  $\langle ff^T \rangle = \langle ff^T \rangle_+ + \langle ff^T \rangle_-$ , leading net of some cancellations to

$$A(t-t') = \langle \dot{x} \dot{x}^T \rangle_{\text{free}} - \langle \dot{x} \dot{x}^T \rangle = G_R^T * \langle ff^T \rangle_- * G_R^T + G * \langle ff^T \rangle_+ * G.$$

It is important to bear in mind that this result already assumes that the underlying noise is time reversible and hence both  $G$  and  $G_R$  are symmetric under  $T$ .

For the instantaneous case considered by Fixman where  $G(t-t') = g\delta(t-t')$ , we have  $G = G_R$  and the above result simplifies down to that of Fixman,

$$\langle \dot{x} \dot{x}^T \rangle_{\text{free}} - \langle \dot{x} \dot{x}^T \rangle = \langle ww^T \rangle$$

where  $w(t) = g f(x(t))$  is the direct contribution to the motion due to the conservative forces.